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The photofading mechanism of commercial reactive dyes on cotton

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Abstract

The photofading mechanism of 16 commercial dyes (8 Procion, 8 Remazol) reactively dyed on cotton is investigated. All 16 dyes fade at similar rates, with ΔE's of 2.7–6.1 after 15 h irradiation in simulated Florida sunlight. By removal of UV, it is shown that fading is caused by both visible and UV light, with visible light being the dominant factor for azo dyes and UV for phthalocyanines. By removal of oxygen, it is shown that oxygen is critical for fading by visible but not UV light. Quenching experiments with DABCO show that singlet oxygen is unimportant, and therefore the key reaction in visible fading is an electron transfer from the excited state of the dye to oxygen. Water in the pH range 3–8 increases fading by only 36% compared to dry and at more extreme pH's, larger increases in fading are seen.

Keywords: Photofading; Photobleaching; Reactive dyes; Electron transfer; Singlet oxygen; Cotton

1. Introduction

The fading of coloured textiles upon exposure to light is a well-known phenomenon, and has been an active area of research for nearly 200 hundred years [1]. The mechanisms by which dyes undergo photodegradation is thought to be complex [2]. However, most of the art suggests that UV light-induced unimolecular decomposition and visible light-induced photo-oxidation are the two most important pathways:

$$\text{dye} + \text{UV light} \rightarrow \text{bleaching} \quad (1)$$

$$\text{dye} + O_2 + \text{light} \rightarrow \text{bleaching} \quad (2)$$

These conclusions arise from work carried out over the last two hundred years, which is briefly summarised below, more extensive reviews are available elsewhere [1,2].

Early work in the 19th century suggested that removal of oxygen prevented photofading [3]. This effect was crystallised by Gebhard in 1910 who showed that coloured fabrics (probably direct dyed cotton) under vacuum did not photofade [4]. From these experiments it was concluded that photofading was an oxidative process. Although Gebhard realised that both UV and visible light were emitted by the sun, it is not clear if the glass vessels used in these studies were transparent to UV and therefore UV effects may have been overlooked. However in 1924, Heerman clearly showed that dyes could be readily photodegraded by UV light [5].

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Following these seminal works many authors have sought to fully understand the chemistry and reactive species involved in photofading. Notably, Egerton in a series of papers showed that reactive oxygen species, ROS, were produced by irradiation of dyed fabrics and these were capable of destroying dyes [6]. The nature of the ROS, i.e. singlet oxygen, hydrogen peroxide, superoxide radicals, hydroxyl radicals or peroxy radicals was not defined. Subsequently a large amount of work has been done on how these species might be formed during irradiation and the damaging effect they have on dyes. Most attention has been paid to singlet oxygen, $^1O_2$, which can be formed by the quenching of excited states of dyes by the triplet ground state of oxygen [7]:

$$\mathrm{dye} \overset{\mathrm{light}}{\rightarrow} \mathrm{dye}^* + {}^3O_2 \overset{\mathrm{quench}}{\rightarrow} \mathrm{dye} + {}^1O_2 \tag{3}$$

Many model studies have shown that singlet oxygen is very reactive towards dyes [8,9], although its importance is unclear. Recent quantitative work has suggested that its role in photofading of azo-dyes is quite small [10,11].

The quenching of excited states of dyes by oxygen has also been shown to lead to the formation of the superoxide radical and destruction of the dye [12]:

$$\mathrm{dye} \overset{\mathrm{light}}{\rightarrow} \mathrm{dye}^* + {}^3O_2 \overset{\mathrm{electron\ transfer}}{\rightarrow} \mathrm{dye}^{\bullet+} + O_2^{\bullet-} \tag{4}$$

The so-formed superoxide could then react and destroy further dye molecules [6].

Clearly, the exact mechanism by which a dye photofades will critically depend on the dye and fibre type. Much of the literature studied employed model systems such as cellulose films or aqueous solutions and it is not clear how the results relate to real world cases. Therefore to understand the relative importance of UV and visible light plus the various possible ROS's to photofading, a study is presented of 16 commercially important reactive dyes on cotton. A quantitative picture of the mechanism of photofading is developed, and the percentage contribution of each pathway is determined.

2. Experimental

2.1. Dye set

Table 1 lists the 16 reactive dyes used in this study alongside their chemical type. In total 8 monochlorotriazine Procion^{TM} HE dyes (ex. BASF), and 8 β-sulphatoethyl sulphone Remazol^{TM} dyes (ex. Clariant) were used, of which 13 were azo dyes (all in the hydrazone tautomer), two were phthalocyanine, and one was a 1:1 mixture of triphenodioxazine and azo. They were chosen to give a representative set of the reactive dyes currently in widespread use [13].

Each dye was printed on to bleached plain-woven cotton fabric in stripes. The dye penetrates approximately one third to one half of the way through the cotton and behaves similarly to fabric that has been conventionally dyed. The dye concentration of the dyed side of the fabric that was exposed to light was approximately 0.25% owf giving a pastel shade. Colour fabric strips containing dyes 9, 12, 16 and a 1:1 mixture of 12 and 16 were also prepared at approximately 2.5% owf (i.e. ten times the concentration), allowing a comparison between light and dark shades. All multi-dye

Table 1
Dye set used

No.	Name	Type	g/kg
Procion			
1	Red HE-7B	Hydrazone	0.5
2	Scarlet HE-3G	Hydrazone	0.5
3	Crimson HE-XL	Hydrazone	0.5
4	Yellow HE-6G	Hydrazone	1.0
5	Red HE-GXL	Hydrazone	0.5
6	Blue HE-XL	Triphenodioxazine and hydrazone	2.0
7	Turquoise H-A	Phthalocyanine	5.0
8	Navy HE-XL	Hydrazone	1.0
Remazol			
9	Red RB	Hydrazone	1.0
10	Golden Yellow RNL	Hydrazone	1.0
11	Brilliant Red RBS	Hydrazone	2.0
12	Yellow FG	Hydrazone	1.0
13	Orange FR	Hydrazone	2.0
14	Navy GG	Hydrazone	2.0
15	Turquoise G	Phthalocyanine	2.0
16	Black B	Hydrazone	1.0

fabric strips were obtained from VeebeeTech and used as supplied.

The liquid benzotriazole UVA & UVB sunscreen, Tinuvin^{TM} 571 and the HALS antioxidant, Tinuvin^{TM} 765 [15] were obtained from Ciba Speciality Chemicals (Basel). 1,4-diazabicyclo[2,2,2]octane (DABCO) and vitamin E, was obtained from Aldrich. All chemicals were used as supplied and applied by padding onto the multi-dyed fabric strips from ethanol.

The dyed fabric stripes were irradiated using a Xenon S3000 Weatherometer (WOM) employing radiation equivalent to average mid day sunlight in Florida. This gives 42 W/m^2 (290–400 nm) in the UV and 343 W/m^2 in the visible (400–800 nm) The humidity was 35% in all experiments. Exposure times of up to 145 h were employed.

To remove UV from the irradiating light, 1% of Tinuvin^{TM} 571 was pad applied to the fabric. Calibration experiments with different levels of the sunscreen showed this shielded the dye from all UV radiation and did not give a change in colour to the dyes. Further experiments showed that the sunscreen was itself photostable over the irradiation periods. Oxygen was removed from the sample by placing the fabric in a UV transparent quartz glass vessel, evacuating using a water pump then sealing. It should be noted this produces a relatively poor vacuum. For proper comparison of the relative effect of UV and oxygen, all these experiments were conducted in the quartz glass vessel.

The colour of the samples, expressed as the CIELAB ΔE value compared to new was determined using a Datacolor Spectraflash SF600 Spectrophotometer.

3. Results and discussion

3.1. Fading and its kinetics

Table 2 shows the photofading of all 16 dyes after 15 h exposure to simulated sunlight in the WOM. Interestingly there is little difference in the fading of the 16 dyes with ΔE only varying between 2.7 and 6.1 and all these values are clearly perceivable by the human eye. Also given in the table is an estimate of the % of dye molecules destroyed, calculated from the reflectance spectrum of the dye, and here a slightly larger variation is found, from 5.8 to 27%.

Table 2
Fading observed after 15 h irradiation. Values are averages of 13 separate experiments

Dye No.	Colour	ΔE_{new} ($\pm$0.4)	% Dye lost
1	Red	5.4	21.6
2	Scarlet	3.8	20.8
3	Crimson	6.1	19.6
4	Yellow	6.1	26.4
5	Red	5.0	13.2
6	Blue	2.7	7.0
7	Turquoise	2.8	5.8
8	Navy	3.7	11.8
9	Red	4.3	11.8
10	Yellow	3.1	27.0
11	Red	4.1	8.4
12	Yellow	3.2	17.3
13	Orange	3.3	9.8
14	Navy	3.5	11.7
15	Turquoise	3.1	13.4
16	Black	3.6	24.8

The kinetics of fading up to 145 h was determined for dyes 9, 12, 16 and a 1:1 mixture of 12 and 16 (giving a green shade) and compared to the fading of cloth dyed with approximately 10 times the level of dye. The average results are presented in Figs. 1 and 2 and as expected the fading increases with time. Interestingly the dark shades show less visible fading than the pastel. For both

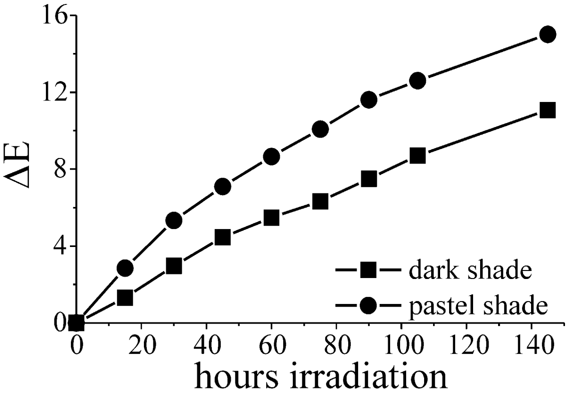

Fig. 1. Average kinetics of fading.

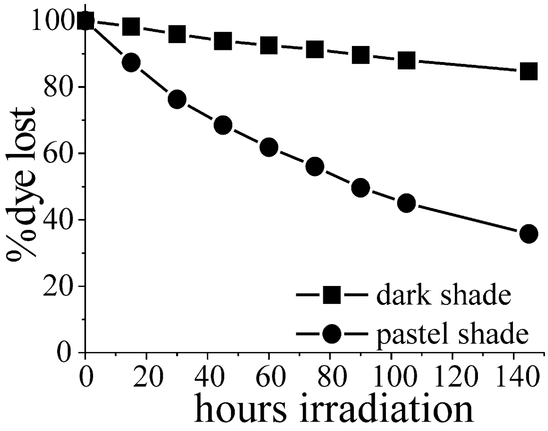

Fig. 2. Average % dye lost with irradiation time.

dye levels, dye is lost approximately linearly with time, over the 145 h, although a much greater percentage of dye is lost with the pastel dyed cloth. When the different amount of dye on the cotton is taken into account then approximately twice as much dye is lost from the dark shade than the light, which can be assigned to a greater absorption of light causing more photobleaching. That the fading is roughly linear with time and there is little difference between dye levels shows that the photofading mechanism does not substantially change with time or with dye level. Thus mechanistic inferences obtained from photofading experiments with short irradiation periods and with pastel shades should be general.

3.2. *The effect of removing UV and oxygen*

The effect of removing UV light, oxygen and UV + oxygen on the photofading of the dyes is given in Table 3 and the average results divided into the two dye classes is given in Fig. 3. In the discussion the average results will be used.

Removal of the UV fraction of the simulated natural light led to a reduction in fading of approximately 20 and 70% for the azo and phthalocyanine dyes respectively. Therefore the visible fraction must be responsible for 80 and 30% of the fading respectively. Consequently both visible and UV light leads to the fading of these dyes but for azo dyes the visible portion is dominant and for phthalocyanines the UV is dominant. This large difference can be assigned to the fundamentally different structures of the dye classes leading to different photochemistry.

Table 3
Effect of removal of UV light, oxygen and UV + oxygen on photofading

Dye No.	Colour	Type	% UV fade reduction	% O_2 fade reduction	% UV + O_2 fade reduction
1	Red	Hydra	23	27	70
2	Scarlet	Hydra	20	46	81
3	Crimson	Hydra	23	26	74
4	Yellow	Hydra	24	42	70
5	Red	Hydra	20	56	69
6	Blue	Triphen/hydra	43	52	75
7	Turquoise	Phthalo	62	5	32
8	Navy	Hydra	6	50	77
9	Red	Hydra	48	15	58
10	Yellow	Hydra	21	36	58
11	Red	Hydra	30	50	60
12	Yellow	Hydra	13	72	83
13	Orange	Hydra	1	32	67
14	Navy	Hydra	29	27	59
15	Turquoise	Phthalo	79	29	67
16	Black	Hydra	36	28	58

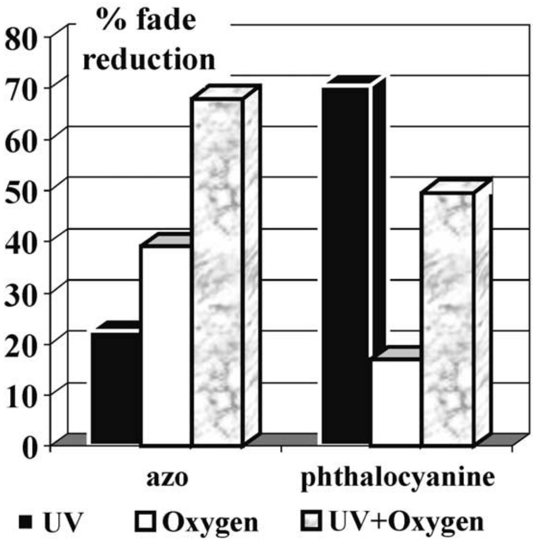

Fig. 3. Maximum % fade reduction effect caused by removal of UV radiation and oxygen.

In the simulated sunlight the UV fraction is a small proportion of the total, there being only 42

W/m^2 of UV light compared to 343 W/m^2 of visible. When this is taken into account, it is clear that the UV light per Watt is more damaging than the visible for all the dyes, i.e. only 12% of the light power is in the UV but the amount of UV photofading is 20 and 70% for the azo and phthalocyanine dyes respectively. To measure these numbers, UV light per Watt must be 2 times as damaging as visible light for azo/hydrazone dyes and 23 times as damaging for phthalocyanines. It is perhaps surprising that the difference is not greater.

Removal of oxygen led to a reduction in the photofading of all the dyes and the effect was greatest for the azo dyes. The values given in the table are underestimates of the effect as only a poor water pump vacuum was used. When UV and oxygen were both removed, an even greater decrease in photofading was seen (the small decrease for phthalocyanines is almost certainly due to experimental error, there being only 2 dyes). Interestingly the effects are additive and not synergistic nor antagonistic such that:

$$\begin{aligned}&\%\ \text{UV} + \text{O}_2\ \text{fade reduction}\\ &\quad = \%\ \text{UV fade reduction}\\ &\qquad + \%\ \text{O}_2\ \text{fade reduction}\end{aligned} \tag{5}$$

If UV and visible fading both require oxygen to occur, then an additive effect would not be seen, as the total UV fraction would be accounted for in both the sunscreen and oxygen experiments. For example, consider a dye which fades 100% in the UV with oxygen then the above experiments would yield reduction of 100% in all experiments and Eq. (5) would not work. Consequently the results show that UV photofading does not require oxygen but visible light photofading does. This fact combined with the different efficiencies of fading calculated above show that the basic chemical mechanism of UV and visible light photofading are different, an important conclusion.

These results are supported by recent patent work, which showed that use of an oxygen barrier with a sunscreen on dyed cotton effectively prevented all photofading. The effect of the oxygen barrier and sunscreen were additive [14], as expected from Eq. (5).

3.3. Identification of oxygen reaction

Visible light fading of dyes could involve oxygen via reaction (3) or (4). The singlet oxygen route involves 2 steps, formation of $^1O_2$ by quenching of the excited state of the dye, then bleaching of the dye by $^1O_2$. These processes will give $^1O_2$ a finite lifetime and means it could be removed by addition of $^1O_2$ quenchers such as DABCO [8]. For the alternative, electron transfer from the excited state of the dye to oxygen, bleaching is seen in one simple step and quenching of this reaction is not possible. If the so-formed radical ions react with further dyes in a chain reaction, some reduction in fading would be expected by addition of a radical scavenger such as HALS, which are widely used in plastics for this purpose [15].

Consequently it should be possible to distinguish between the two routes by addition of DABCO, which will only effect the fading if $^1O_2$ is important. Additionally to understand if radical chain process are involved a HALS can be added. In such experiments it is important to know if surface effects alter the chemicals behaviour in cotton. Fortunately a number of recent studies of radicals and singlet oxygen in cotton have shown that their chemistry is similar to solution [16–18].

Addition of DABCO and a HALS at 0.05 and 0.1% on weight of fabric followed by irradiation for 15 h gave no reduction in the fading of any of the dyes. Thus electron transfer to oxygen is the main photobleaching process occurring with visible light for these dyes. Radical chain reactions are not initiated by this process. In hindsight, the lack of importance of $^1O_2$ is perhaps not surprising, as the dyes used in the current study are thought to have extremely short excited state lifetimes, in the picosecond range [19,20]. This means that the quantum yield for formation of $^1O_2$ and electron transfer will be very small [21]. For bleaching by $^1O_2$ to occur, the $^1O_2$ must react with dye before it is quenched by the environment. The amorphous regions of cotton where the reactions take place, contain a large amount of water [22] which can efficiently quench $^1O_2$ lifetime in water is only 4 microseconds [8] and therefore very little $^1O_2$ is formed and what is formed is rapidly removed by the environment. Interestingly Kiwi and Bandera recently reached a similar conclusion for the simple azo-dye, Orange II, in aqueous solution [12].

3.4. *Effect of moisture*

All the work in Sections 1.1–1.3 was carried out on dry cotton. To investigate if moisture would substantially change the results, a comparison of the fading of dry and wet cotton was conducted. The experiment was carried out by irradiating the cotton in a quartz glass bath filled with water and then repeating the experiment in an empty bath. Unfortunately the results were quite noisy, making detailed interpretation by dye class difficult; however the average fading of the 16 dyes was increased by 36%.

Water with buffered pH's in the range 2–9 were also applied and the results shown in Fig. 4. No significant effects were noted except at pH 2 and 9 where very large increases in fading were observed. Control experiments where the cloth was left in water in the dark showed no fading, except for pH 2 and 9, were some small fading effects were noticed after 15 h soaking. Consequently in the pH range 3–8 wet fabric fades faster than dry, but the difference although substantial is not huge. This suggest that the fading mechanism is not greatly altered by moisture in this range, however at more extreme pH's large changes occur.

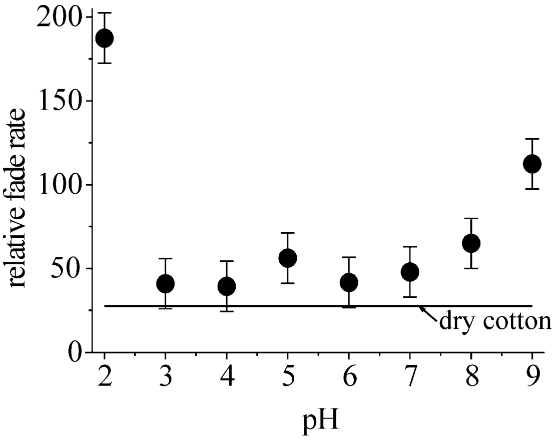

Fig. 4. Average relative fade rate (arbitrary units) of the 8 remazol dyes on wet cotton as a function of the pH of the water. The procion dyes showed a similar dependence.

4. Conclusion

The photofading of commercial reactive dyes on cotton is due to both UV and visible light, with the relative importance being determined by the dye type. For the very popular azo/hydrazone dyes, visible light is the most important contributor under normal lighting conditions. Oxygen is required for visible but not UV fading of the dye indicating two mechanisms of photodegradation. Wetting the fabric does not greater increase the rate of photofading, except at high (>9) or low ($3<$) pH.

It would be interesting and informative to expand the current study to include other dyed substrates such as paper, wool and polyester, to see if similar factors control their photofading.

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